

The University of Chicago

I. THE STABILITY OF THE CARBON-TO-CARBON
BOND

II. THE INFLUENCE OF SALT FORMATION ON
THE STABILITY OF THE CARBON-TO-NITROGEN
BOND OF CERTAIN SUBSTITUTED
METHYL AMINES

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1933

By

JULIUS D. PORSCHE

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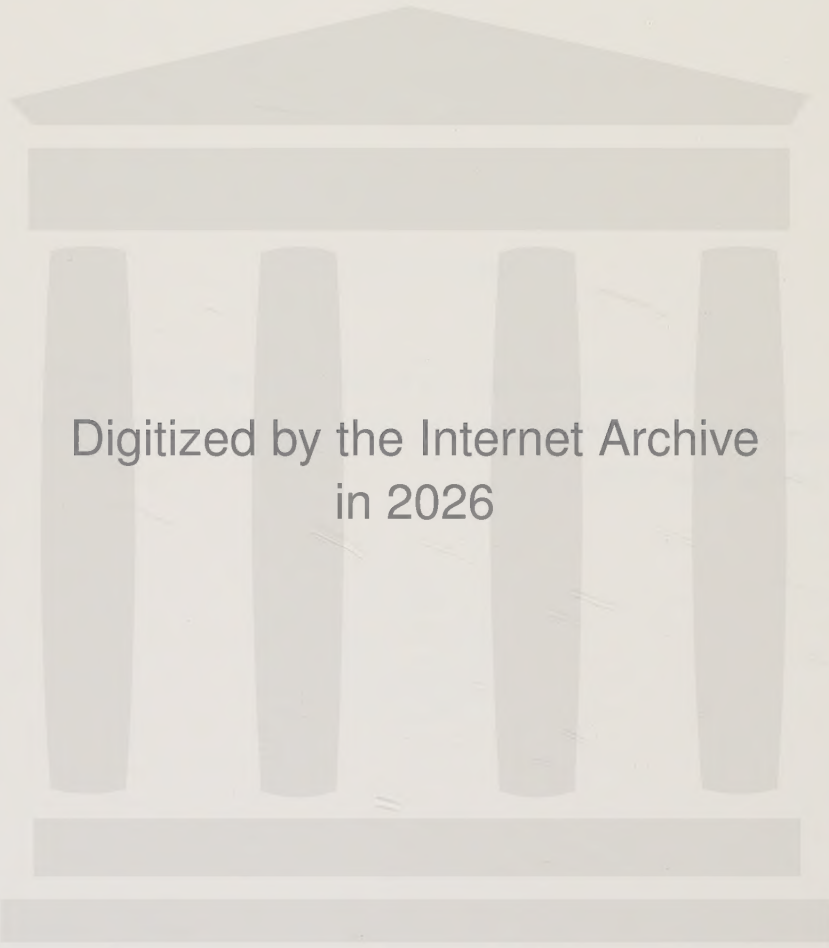
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I. THE STABILITY OF THE CARBON-TO-CARBON BOND

Kharasch and Reinmuth¹ have called attention to the fact that the stability of a carbon-to-carbon bond is not a function simply of its polarity or non-polarity, but of the affinity of the carbon atoms for the binding electrons. Accordingly, the various types of carbon-to-carbon bonds are represented as follows:

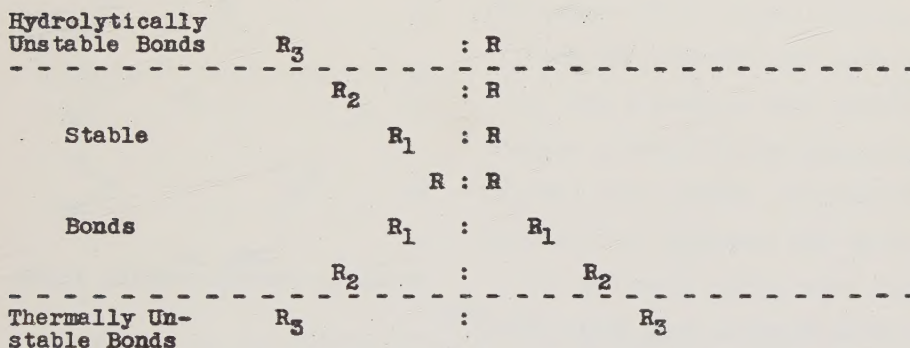


Fig. 1. Types of Carbon-to-Carbon Bonds

Briefly, a high degree of electron affinity (i.e. electronegativity) on the part of both carbon atoms results in marked stability of the linkage between them, whereas a low degree of electronegativity on the part of either or both of the carbon atoms effects a diminution in the strength of the bond. If there is a sufficient difference in the electronegativities of the two carbon atoms, the bond will exhibit polar characteristics such as

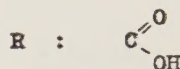
1. Kharasch and Reinmuth, J. Chem. Educ., 5, 409 (1928)

hydrolytic instability. If both carbon atoms are very weakly electronegative the bond between them may be decidedly non-polar, and yet exhibit marked thermal instability.

Consideration of the thermal and hydrolytic stability of the bond between any radical R and the weakly electronegative carboxyl group furnishes an excellent illustration of the concept.² For the purpose of discussion, the number of representative types of the bond may be reduced to three: 1. R is neither strongly nor weakly electronegative. 2. R is very strongly electronegative. 3. R is very weakly electronegative.

Organic acids of type 1.

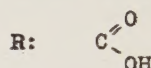
are relatively stable compounds. 1.



Indeed they possess the most

stable bond between R and the

2.



carboxyl group found in organic

molecules. Benzoic and acetic

3.



acids are examples of this type,

and lose carbon monoxide and

carbon dioxide only under most

Fig. 2.
Types of Monocarboxylic Acids

drastic conditions. Acids of type 2. are characterized by marked instability toward hydrolytic reagents and undergo double decomposition reactions of various kinds, such as the reaction of certain phenol carboxylic acids with diazonium salts producing azo compounds and carbon dioxide. The polar nature of the bond is further attested to by the absence of carbon monoxide as a decomposition product, regardless of the reagent used to rupture the bond. Acids of type 3. are also exceedingly unstable but evidence of polarity in the bond is lacking. Both carbon monoxide

2. Kharasch and Reinmuth deal exhaustively with this topic in a paper as yet unpublished.

and carbon dioxide are found when the bond is ruptured, since neither carbon atom has a decided affinity for the electrons. The triaryl acetic and substituted glyoxylic acids are examples of this type.

Further experimental verification of their view has been made possible by the following postulate advanced by Kharasch and Reinmuth.¹ The substitution of a comparatively electronegative group, such as phenyl, for a hydrogen atom in methane, decreases the electronegativity of the methane carbon atom.

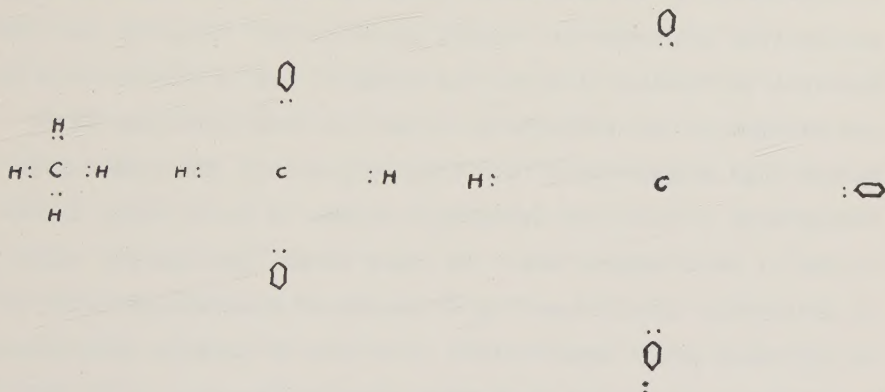


Fig. 3.

The Effect of the Substitution of Electronegative Groups on the Electron Configuration of Methane

In other words, such a substitution induces a general outward displacement of the electron doublets constituting the octet of the methane carbon atom. The magnitude of this displacement depends on the number and the electronegativity of the substituted groups. By linking two of the methane carbon atoms to one another, an opportunity is afforded of studying the effect of changing their electron affinities on the thermal stability of the bond uniting them. Similarly, the introduction of sufficiently strongly electronegative groups into the methane nucleus should provide a means of forming markedly polar carbon-to-carbon bonds.

Kharasch and Marker³ have shown that the variations in the observed thermal stabilities of the hexa-aryl ethanes coincide with those required by the postulate previously stated. Indeed, application of the notion to the problem has done much to correlate and explain the data concerning the dissociation of molecules of this type. It is clear, from examination of these data, that as the electronegativity of two carbon atoms joined by a single bond is decreased, a certain liminal value of electronegativity is reached below which further decreases result in perceptible increases in thermal instability. Dibenzyl and symmetrical tetraphenyl ethane, for example, can be distilled without decomposition, pentaphenyl ethane is disproportionated at rather high temperatures into triphenyl-methyl and symmetrical tetraphenyl ethane, and hexaphenyl ethane is perceptibly dissociated at room temperature. In other words, the liminal value of electronic displacement or of decreased electronegativity of two mutually bound carbon atoms necessary to produce spontaneous instability at ordinary temperatures cannot be reached by the substitution of two phenyl groups for hydrogen atoms in each methyl group, whereas it is exceeded by the substitution of three phenyl groups. Any additional increase in the electronegativity of the groups attached to the methane carbon atoms still further increases the instability of the molecule, and consequently the degree of dissociation.

On the other hand, the literature contains but little evidence for the existence of markedly polar carbon-to-carbon bonds. Kostanecki and Zibell⁴ have shown that p-hydroxy benzoic acid undergoes metathesis with phenyl diazonium chloride and

3. Kharasch and Marker, J. Am. Chem. Soc., 48, 3130 (1926)

4. Kostanecki and Zibell, Ber., 24, 1695 (1895)

forms p-hydroxy azobenzene. Nietzki and Guiterman⁵ demonstrated that while β-hydroxy α-naphthoic acid behaves in an analogous manner with phenyl diazonium chloride, α-hydroxy β-naphthoic acid coupled with the diazonium salt without loss of carbon dioxide. A few instances are also available in which evidence of polarity among the polyaryl methanes has been obtained. For example, Moehlau and Strohbach⁶ proved that di-β-naphthol methane is decomposed by phenyl diazonium chloride with the formation of formaldehyde and benzene azo-β-naphthol. A perfectly analogous reaction occurs between phenyl diazonium chloride and the condensation product of formaldehyde and dimethyl phloroglucinol.^{7,8} Of course numerous reactions involving scission of a carbon-to-carbon bond occur at high temperatures and under the influence of vigorous reagents which may be explained by assuming ionization of the carbon-to-carbon bond and subsequent hydrolysis. The mechanism of these reactions is, however, frequently obscure. On the other hand, true evidence of marked polarity of carbon-to-carbon bonds, e.g., metatheses induced by mild reagents at moderate temperatures - below 100° or 150° - is, as has been shown, very rare.

Marked changes in the electronegativity of the substituents in methane derivatives may be made without producing perceptible evidence of polarity. For example, no differences in hydrolytic instability can be demonstrated between tetraphenyl and tetramethyl methane. However, in view of the sudden appearance of thermal instability in the ethane molecule upon the sub-

5. Nietzki and Guiterman, Ber., 20, 1274 (1887)

6. Moehlau and Strohbach, Ber., 33, 804 (1900)

7. Boehm, Ann., 318, 259 (1901)

8. When this investigation was near completion, Brass and Fiedler (Ber., 65B, 1654 [1932]) published evidence for the hydrolysis of benzalbis (β-hydroxynaphthoic acid) in alkaline solution.

stitution of the fifth phenyl group, it is reasonable to suppose that there is a liminal value of electronic displacement or decreased electronegativity of the methane carbon atom which must be exceeded before evidence of polarity may be obtained with the aid of mild chemical reagents.

Accordingly, a preliminary investigation has been undertaken to determine whether or not such a threshold may be reached, and to pave the way for a more exhaustive study of the properties of markedly polar carbon-to-carbon bonds.

The first requisite for the project was a molecule or group containing a powerfully electronegative carbon atom. A clue was obtained from the study by Kharasch and Howard⁹ of the stability of the carbon-to-nitrogen bond. The course of hydrolysis of α -amino benzyl 1-naphthol-2 leads to the conclusion that the α carbon atom of β -naphthol is very strongly electronegative, having an induced effect on the electronic configuration of the methane carbon atom of the same order as that of the amino group. The molecular type $R-\overset{H}{C} = \left(\text{O}^{\cdot\cdot} \right)_2$ therefore suggested itself as a convenient one for study, due to the possibility of wide variation in the electronegativity of the group R. Similarly, the hydrolysis of triphenyl-methyl amine led to the supposition that triphenyl-methyl 1-naphthol-2 might undergo an analogous decomposition in the presence of hydrolytic agents.

Hydrochloric acid was chosen as the hydrolytic agent because of its strongly acid and exceedingly feeble reducing properties. Acetic acid has been used as a solvent for convenience in manipulation and isolation of the molecules studied and their decomposition products.

9. Kharasch and Howard, unpublished work.

RESULTS

The series of molecules listed in the accompanying tables have been constructed and the various members have been subjected to treatment with two percent hydrochloric acid in boiling glacial acetic acid.

Two distinct reactions occur almost instantaneously. These are illustrated by the following equations:



The chief reaction is that involving scission of the carbon-to-carbon bond. The results obtained are summarized in Table I.

With a view to preventing dinaphthopyran formation and demonstrating that the observed scission is that of a carbon-to-carbon and not that of a carbon-to-oxygen bond, the dimethyl ethers of these molecules have been prepared and subjected to the same treatment. Rupture of the carbon-to-carbon bond was again observed with consequent formation of an aldehyde and methyl ether of β -naphthol. The extent of formation of the methyl ether of β -naphthol corresponding to variations in the group R is recorded in Table I.

The dinaphthopyrans were not affected by two percent hydrochloric acid.

Four tetra-aryl methanes: triphenyl-methyl - phenol, re-

sorcinol, resorcinol dimethyl ether and β -naphthol have been subjected to the same treatment without obtaining evidence of decomposition.

Further evidence for the marked polarity of the dinaphthol methane derivatives has been obtained by allowing them to react in acetic acid solution at room temperature, with the anti-diazotate of 2,5 dichloraniline - a relatively stable diazo compound. They are found to react at varying rates with this reagent, depending on the nature of the group R in accordance with the following equation:



Triphenyl-methyl naphthol does not undergo decomposition under these conditions but couples, as a unit, with the diazo compound. The results of the experiments performed are presented in Table 2.

Table 1.
Extent of hydrolysis of the di- β -naphthol
methanes and their dimethyl ethers

R	$\text{R}-\text{C}^{\text{H}} = (\text{OH})_1$			$\text{R}-\text{C}^{\text{H}} = (\text{OCH}_3)_2$
	C-C scission in mol %	Pyran Formation	Unchanged material	C-C scission in mol %
$(\text{CH}_3)_2\text{N}-\text{C}_6\text{H}_4-$	15%	?	?	Not prepared
$\text{CH}_3\text{O}-\text{C}_6\text{H}_4-$	35%	?	?	45%
C_6H_5-	50%	20%	30%	45%
$\text{NO}_2-\text{C}_6\text{H}_4-$	30%	10%	40%	10%
$\text{NO}_2-\text{C}_6\text{H}_3-$	5%	5%	85%	trace
$\text{C}_6\text{H}_5-\text{C}^{\text{H}}(\text{H})-\text{C}^{\text{H}}(\text{H})-\text{C}_6\text{H}_5$	35%	?	?	35%
H	5%	15%	80%	5%
$\text{Cl}_3-\text{C}-$		Not prepared		none
Benzyl 1-naphthol-2	none		100%	Not prepared

Table 2.

Yields of 2,5 dichlorobenzene azo-*p*-naphthol obtained by treatment of the di-*p*-naphthol methanes with the anti-diazotate of 2,5 dichloraniline.

R	% Yield	M.P.
<chem>CH3c1ccc(cc1)-</chem>	80%	170-3
<chem>c1ccccc1-</chem>	48%	171-4
H-	47%	155-65
<chem>c1ccc(cc1)C(C)(C)c2ccccc2</chem>	64%	170-5
<chem>c1ccc(cc1)[N+](=O)[O-]</chem>	49%	160-5
<chem>c1ccc(cc1)[N+](=O)[O-]</chem>	0%	
<chem>(CH3)3Nc1ccc(cc1)-</chem>	0.75g.	125-35
<i>β</i> -naphthol	96%	177-9

DISCUSSION

The results obtained demonstrate strikingly the necessity of exceeding a certain threshold of decreased electronegativity of the methane carbon atom before it is possible to obtain perceptible evidence of marked polarity. The stability of the tetra-aryl methanes seems to indicate that three phenyl groups and one 4-hydroxy-phenyl or 2,4 dihydroxy-phenyl group are insufficient to induce the liminal magnitude of electronic displacement. Similarly, one phenyl and one naphthol group are insufficient, as evidenced by the stability of benzyl 1-naphthol-2 toward the reagents employed. One might go farther and conclude, from the stability of triphenyl-methyl naphthol to two percent hydrochloric acid, that three phenyl groups and one naphthol are also insufficient were it not for the observation that the molecule couples, as a whole, with the diazo reagent. This reaction suggests the possibility that the α position of the naphthol group is free and that the structure is not triphenyl-methyl

1-naphthol-2 as proposed by Hardy.^{10,11} Two naphthol groups and two hydrogen atoms, however, as in di- β -naphthol methane, are just sufficient to exceed the liminal value of electron displacement. Two percent hydrochloric acid produces a scission of the carbon-to-carbon bond that is just perceptible as indicated in Table 1., and a more striking indication is obtained by removing β -naphthol as 2,5 dichlorobenzene azo β -naphthol and displacing the equilibrium as shown in Table 2. Further decrease in the electronegativity of the methane carbon atom by the substitution of a strongly electronegative group for one of the remaining hydrogen atoms in di- β -naphthol methane results in greater hydrolytic instability of the bonds between the naphthol groups and the methane carbon atom. The very weakly electronegative ortho-nitro phenyl and trichlormethyl groups were the only substituents employed which did not enhance the polarity of the molecule.

Examination of the data indicates a lack of exact parallelism between the electronegativity of the group R and the extent of carbon-to-carbon scission. A consideration of the reactions which occur simultaneously with the scission of the carbon-to-carbon bond will demonstrate that the lack of parallelism in no way invalidates the postulate previously advanced.

Once the threshold of decreased electronegativity of the methane carbon atom is passed, a highly complex interplay of reversible and irreversible reactions determines the amount of β -naphthol formed by hydrolysis of the substituted dinaphthol methane. For example, β -naphthol reacts with aldehydes, forming

10. Hardy, J. Chem. Soc., 1929, 1000

11. At this point, attention should be called to the fact that no conclusive evidence has as yet been presented to show that when a fourth aryl group is introduced into a tri-substituted methane molecule, it becomes attached to the methane carbon atom rather than to one of the aryl groups.

the original compound or an acetal, the stability of which depends on the group R. The acetal may undergo hydrolysis or rearrangement either to the original compound or to the corresponding dinaphthopyran. It is highly probable that rearrangement of the acetal may result in linkages of the methane carbon atom to positions other than α on the naphthol nucleus with consequent stabilization of the molecule. Furthermore, carbinol formation is undoubtedly an intermediate step in the hydrolytic process. The carbinols are capable of rearrangement to colored quinoid derivatives of unknown stability, and are acetylated with varying ease. Finally, another complication is added when the group R is very strongly electronegative, such as anisyl or p-dimethylamino phenyl, due to the enhanced susceptibility of the bond linking R and the methane carbon atom to hydrolysis.

The dimethyl ethers, on the other hand, yield more satisfactory results, since methylation not only eliminates reactions due to the phenolic hydroxyl group but also decreases the electronegativity and consequently the reactivity of the α carbon atom of the naphthol nucleus. As a result, the possibility of acetal and dinaphthopyran formation is eliminated, and the tendency of the decomposition products to recondense is decreased.

Similarly, the reactions of the dinaphthol methanes with the diazo salt yield results quite in accord with the concepts outlined.

In order to demonstrate that the carbon-to-carbon scission is of a hydrolytic rather than a thermal nature, two grams of benzal di- α -naphthol were subjected to the same treatment that led to fifty percent decomposition, except that the hydrochloric acid addition was omitted. The dinaphthol methane was quantitatively recovered. Similarly, anisal di- α -naphthol dimethyl ether was

unchanged after heating in benzene solution at 150° for five hours.

EXPERIMENTAL PART

PREPARATIONS

The Di-β-naphthol Methanes:

p-Dimethylamino-benzal di-β-naphthol.- The method of Hewitt, Turner and Bradley¹² for the preparation of the hydrochloride was employed with but slight modification. Seven and five-tenths g. of p-dimethylamino benzaldehyde and 14.4 g. of β-naphthol were dissolved in 80 c.c. of glacial acetic acid. After the addition of 10 c.c. of concentrated hydrochloric acid, (sp. gr. 1.18), the walls of the container were vigorously rubbed with a glass rod. The rubbing was repeated at intervals for two days, the container, meanwhile, being tightly stoppered and in an ice chest. After three days the condensation was complete.

The white crystalline product was collected on a filter and washed thoroughly with glacial acetic acid, and with water. The hydrochloride was made into a paste with acetone and treated with an excess of a saturated solution of sodium bicarbonate. The free base was extracted with an ether-acetone mixture. Evaporation of the dry (sodium sulfate) solution yielded a brown solid from which a snow white crystalline solid was obtained by repeated crystallizations from alcohol. Yield - 50-60%. M.P. - 175-6° (dec.)

Anal. Calcd. for C₂₉H₂₅O₂N: C, 83.01; H, 6.01

Found: C, 82.90, 82.89; H, 6.35, 6.29

p-Methoxybenzal di-β-naphthol.- Thirteen and six-tenths g. of anisaldehyde and 28.8 g. of β-naphthol were dissolved in

12. Hewitt, Turner and Bradley, J. Chem. Soc., 81, 1207 (1902)

130 c.c. of glacial acetic acid. The solution was cooled to about 5° and treated with 4 c.c. of concentrated hydrochloric acid. The solution was kept at 5° in a tightly stoppered flask. The walls of the flask were rubbed, from time to time, with a glass rod. After 48 hours the precipitate was collected on a filter and washed thoroughly with 70% acetic acid. The product was crystallized twice by the addition of water to its boiling alcoholic solution until crystallization commenced. The substance was completely soluble in 2% NaOH. Yield - 60%. M.P. - 190-2° (dec.)

Anal. Calcd. for $C_{28}H_{22}O_3$: C, 82.73; H, 5.46

Found: C, 82.40, 82.16; H, 5.74, 5.66

Benzal di-β-naphthol.- The following modifications of Hewitt and Turner's¹³ procedure facilitated the isolation of a pure product: Condensation was allowed to take place at 5° and 0.1% sodium acetate is added to the glacial acetic acid used for recrystallization.

The M.P. observed was 203-4° (dec.)

o - and m-Nitrobenzal di-β-naphthols.- Great difficulty was experienced in the isolation of products free from the corresponding nitrophenyl dinaphthopyrans. This difficulty may be obviated by mixing the reagents and permitting the condensation to proceed at a temperature not above 10° and not below 5°. Furthermore, the rate of addition of the condensing agent must be slow in order to avoid local heating effects. o-nitrobenzal di-β-naphthol is very sensitive to light and must be kept in the dark. Observation of these precautions made it possible to duplicate the results of Dischendorfer.¹⁴

o-nitrobenzal di-β-naphthol - M.P. - 205-7° (dec.)

m-nitrobenzal di-β-naphthol - M.P. - 182-3° (dec.)

13. Hewitt and Turner, Ber., 34, 202 (1901)

14. Dischendorfer, Monatsh. Chem., 48, 543 (1927); 49, 137 (1928)

γ -Phenylpropional di- β -naphthol.- All efforts to synthesize this molecule by direct condensation of hydro-cinnamaldehyde with β -naphthol led almost exclusively to products insoluble in alkali. The following procedure, however, affords a satisfactory yield of the pure dinaphthol methane:

Twenty-six and two-tenths g. of γ -phenyl α -(1-naphthol-2) propyl, γ -phenyl propylidene amine¹⁰ and 40 g. of β -naphthol were dissolved in a minimum quantity of boiling benzene in a one-liter beaker. The temperature of the mixture was kept between 90° and 100° for ten hours. Completion of the reaction was recognized by triturating a sample of the gum with cold alcohol. The Schiff base is very insoluble in cold alcohol and separates as white needles if present in appreciable quantities.

When the reaction was complete, the brown gum was extracted four times with one-liter portions of boiling water. The residue was dissolved in about two hundred and fifty c.c. of cold acetone, and treated with seven hundred and fifty c.c. of two percent sodium hydroxide. A small amount of insoluble material was removed by filtration. Acidification of the filtrate precipitated an oil which solidified on standing for a short time. The latter was subjected to three crystallizations from alcohol by the addition of sufficient water to produce a permanent turbidity at the boiling point. This treatment yielded a tan colored crystalline substance. Two crystallizations from toluene were sufficient to remove all the color from the compound. The product was completely soluble in dilute NaOH. Yield - 60-65%. M.P. - 172-3° (dec.)

Anal. Calcd. for $C_{29}H_{24}O_2$: C, 86.10; H, 5.98

Found: C, 85.82, 86.08; H, 6.45, 6.23

Di- β -naphthol methane.- No difficulty was met in prepar-

ing this molecule according to the directions of Abel.¹⁵ The crude product was crystallized twice from boiling toluene. M.P. - 199-200° (dec.)

Benzyl 1-naphthol-2.- Fourteen and four-tenths g. of β -naphthol were dissolved in 300 c.c. of dry toluene. The solution was heated to boiling. After the addition of 2.3 g. of metallic sodium, boiling was continued for five hours. At the end of this time, the metal had disappeared. Twelve and six-tenths g. of benzyl chloride were added to the solution and reflux was continued for two hours. The precipitated solid was separated from the toluene solution by filtration, and extracted with ether. The ether extract was evaporated to dryness together with the toluene solution. The residue was dissolved in a minimum quantity of acetone. A large excess of 2% sodium hydroxide was added and the resulting solution was separated from the precipitated gum by filtration with talc. Acidification of the filtrate precipitated a red-brown solid which was crystallized twice from dilute alcohol, twice from toluene and once from chloroform-ligroin. The product was free of β -naphthol as indicated by the absence of color when mixed with a solution of the anti-diazotate of 2,5 dichloraniline. Yield - 30%. The M.P. - 111-2° - agreed with that recorded by Claisen.¹⁶

The Dimethyl Ethers of the Di- β -naphthol Methanes:

With the exception of trichloroacetal di- β -naphthol dimethyl ether, all the dimethyl ethers were prepared in the following manner:

A ten percent solution of the dinaphthol methane in acetone was vigorously stirred. Two percent sodium hydroxide and methyl sulfate (four moles of each) were added from dropping fun-

15. Abel, Ber., 25, 3214 (1892)

16. Claisen, Z. Angew. Chem. 36, 478 (1923)

nels in such a way that the solution remained faintly alkaline. The resulting mixtures were stirred for one hour to permit completion of the reaction. The products were precipitated by addition of water and redissolved in acetone. Four more moles of sodium hydroxide and methyl sulfate were added and the products were precipitated completely with water. These substances were invariably very pure, although not always crystalline.

p-Methoxybenzal di- β -naphthol dimethyl ether.- The product was crystallized from glacial acetic acid. M.P. - $194-5^{\circ}$.

Anal. Calcd. for $C_{30}H_{26}O_3$: C, 82.90; H, 6.04

Observed: C, 82.89, 82.66; H, 6.12, 6.14

Benzal di- β -naphthol dimethyl ether.- The product was crystallized from glacial acetic acid. M.P. - 184° .

Anal. Calcd. for $C_{29}H_{24}O_2$: C, 86.10; H, 5.98

Observed: C, 86.00, 85.89; H, 5.97, 5.90

m-Nitrobenzal di- β -naphthol dimethyl ether.- Dilute acetic acid was used to crystallize this compound. The observed M.P. was $172-3^{\circ}$, whereas Dischendorfer¹⁵ reported a M.P. of 216°

Anal. Calcd. for $C_{29}H_{23}O_4N$: C, 77.47; H, 5.16

Found: C, 77.69, 77.39; H, 5.92, 5.97

o-Nitrobenzal di- β -naphthol dimethyl ether.- The solvent used for crystallization was again dilute acetic acid. The observed M.P. was $196-7^{\circ}$, whereas Dischendorfer¹⁵ reported a M.P. of 191° .

α -Phenylpropional di- β -naphthol dimethyl ether.- The product was crystallized from alcohol. M.P. - $146-7^{\circ}$.

Anal. Calcd. for $C_{31}H_{28}O_2$: C, 86.09; H, 6.53

Found: C, 86.00, 86.05; H, 6.60

Di- β -naphthol methane dimethyl ether.- M.P. - $146-7^{\circ}$, whereas Kohn and Osterstetzer¹⁷ report $144-5^{\circ}$.

17. Kohn and Osterstetzer, *Monatsh. Chem.*, 39, 302 (1918)

α -trichloroacetal di- β -naphthol dimethyl ether.- Eight g. of methyl ether of β -naphthol and four g. of chloral hydrate were dissolved in 15 c.c. of glacial acetic acid. While the solution was kept at 40-50°, 20 c.c. of concentrated sulfuric acid were added dropwise. The mixture was allowed to stand for thirty minutes. The resulting dark green tar was extracted thoroughly with warm water and alcohol. After standing three or four days, crystallization began. The mass was triturated with a small amount of acetone to separate the tar from the crystals. The latter were collected on a filter and washed with a small amount of acetone. Recrystallization from a large volume of alcohol yielded a pure product. Yield - 20%. M.P. - 182°.

Anal. Calcd. for $C_{24}H_{19}O_2Cl_3$: Cl, 23.88

Found: Cl, 24.0

The Dinaphthopyrans:

Benzal di- β -naphthyl ether.- This substance was prepared according to the method of Claisen.¹⁸

Anisal di- β -naphthyl ether.- This compound was prepared according to the method of Rogow.¹⁹

The Tetra-aryl Methanes:

p-triphenyl-methyl phenol.- The method of Gomberg and Kamm²⁰ was employed for the preparation of this substance.

Triphenyl-methyl - resorcinol, resorcinol dimethyl ether, and β -naphthol.- These compounds were prepared according to the directions of Hardy.¹¹

HYDROLYSES

The Di- β -naphthol Methanes:

The following method has been adopted for a comparative

18. Claisen, Ann., 237, 265 (1887)

19. Rogow, Ber., 33, 3535 (1900)

20. Gomberg and Kamm, J. Am. Chem. Soc., 39, 2014 (1917)

study of the extent of carbon-to-carbon scission in the presence of two percent hydrochloric acid:

Two grams of each compound were dissolved in fifty c.c. of boiling glacial acetic acid. The source of heat was removed and, when ebullition ceased, two and four tenths c.c. of hydrochloric acid (sp. gr. 1.18) were added with agitation of the solution. The resulting mixture was dropped into one hundred and fifty c.c. of boiling water through which a rapid current of steam was passing. The rate of addition was such that three to five minutes were required for its completion. Distillation was continued for ten to fifteen minutes.

Benzal di- β -naphthol.- The steam distillate was collected in a flask containing one c.c. of phenylhydrazine dissolved in a little glacial acetic acid. After two hours, 0.49 g. of benzaldehyde phenylhydrazone (M.P. - 154-5⁰) were obtained by filtration of the distillate.

The suspension remaining in the distillation flask was removed by filtration while the mixture was hot, and dissolved in acetone. The addition of an excess of two percent sodium hydroxide to the acetone solution precipitated 0.40 g. of a crystalline substance which was identified as benzal di- β -naphthyl ether. Acidification of the alkaline solution yielded 0.52 g. of benzal di- β -naphthol. Neutralization of the dilute acetic acid from the distillation flask and subsequent saturation with sodium chloride precipitated 0.77 g. of nearly colorless crystals (M.P. - 117-20⁰) which were identified as β -naphthol.

p-dimethyl amino benzal di- β -naphthol.- None of the starting material or the corresponding dinaphthopyran could be isolated from the brown gum which remained in the distillation flask.

Neutralization of the supernatant dilute acetic acid solution and saturation with salt yielded a small quantity of a green gum from which 0.20 g. of β -naphthol were obtained by extraction with boiling water containing Norite.

p-methoxy benzal di- β -naphthol.- None of the starting material could be isolated from the red gum that remained in the distillation flask. It was possible, however, to obtain 0.18 g. of colorless needles which were identified as p-methoxy benzal di- β -naphthyl ether.

The dilute acetic acid solution yielded 0.60 g. of a red-brown crystalline substance - M.P. - $114-19^{\circ}$. Extraction of the solid with ten percent sodium hydroxide left 0.05 g. of a light brown colored solid of unknown constitution - M.P. - $240-3^{\circ}$. Acidification of the alkaline extract precipitated 0.45 g. of β -naphthol. M.P. - $118-20^{\circ}$.

m-nitro benzal di- β -naphthol.- The alkali insoluble fraction of the gum remaining in the distillation flask weighed 0.23 g. and was identified as m-nitro phenyl di- β -naphthopyran. The alkali soluble portion yielded 0.90 g. of the starting material and a small quantity of gum that resisted all efforts at purification.

β -naphthol (0.42 g.) were obtained in the manner previously described.

o-nitro benzal di- β -naphthol.- o-nitro benzal di- β -naphthyl ether (.07 g.) were obtained by the usual technique from the red-brown gum in the distillation flask. The alkali soluble fraction contained 1.70 g. of the starting material contaminated with a dark tarry impurity which could be removed only by repeated crystallization from acetic acid.

A small amount of red gum was obtained from the hot solu-

tion contained in the distilling flask. Two crystallizations from water (Norite) resulted in the isolation of 0.01 g. of β -naphthol. M.P. - $118-20^{\circ}$.

β -phenyl propional di- β -naphthol.- Repeated crystallizations of the alkali insoluble fraction of the residual yellow gum from benzene-alcohol yielded 0.07 g. of a white crystalline substance (M.P. - 173°) which was assumed to be β -phenyl propional di- β -naphthyl ether.

Anal. Calcd. for $C_{29}H_{22}O$: C, 90.11; H, 5.74

Found: 89.51, 89.86; H, 6.07, 6.13

It was impossible to separate the alkali soluble fraction into its constituents.

The usual treatment of the dilute acetic acid solution yielded 0.48 g. of β -naphthol.

Di- β -naphthol methane.- A little alkali insoluble material (0.28 g. - M.P. - $183-90^{\circ}$) were obtained from the residue in the distillation flask. It was identified as dinaphthopyran. Most of the starting material (1.48 g.) was recovered.

A small quantity of semicrystalline material (0.15 g.) was obtained upon neutralization of the dilute acetic acid. Extraction with hot water yielded .055 g. of β -naphthol and re-crystallization of the residue from alcohol-water left .08 g. of the original material.

Benzyl 1-naphthol-2.- The benzyl 1-naphthol-2 was practically quantitatively (1.97 g. - M.P. - $112-13^{\circ}$) recovered. Treatment with an aqueous solution of the anti-diazotate of 2,5 dichloraniline proved the absence of β -naphthol in the distillate and in the distilling flask.

The Di- β -naphthol Methane Dimethyl ethers:

The same hydrolytic procedure was followed as in the case

of the di- β -naphthol methanes except that steam distillation was continued until no more methyl ether of β -naphthol appeared in the distillate. Two grams were used in each experiment.

Benzal di- β -naphthol dimethyl ether.- Extraction of the residual tar with ether yielded 0.26 g. of crystalline material - M.P. - $170-6^{\circ}$. This was identified as the starting material. All attempts to separate the remaining resinous substance into its constituents failed.

Seven hundred milligrams of the methyl ether of β -naphthol were obtained from the distillate.

Anisal di- β -naphthol dimethyl ether.- None of the starting material could be obtained from the residual gum.

The distillate yielded 0.65 g. of the methyl ether of β -naphthol.

m-nitro benzal di- β -naphthol dimethyl ether.- Fractional crystallization of the residual material from acetone-water mixtures resulted in the recovery of 1.35 g. of the starting material. The remainder of the residue was a brown oil containing a small amount of m-nitro benzaldehyde.

The distillate yielded 0.13 g. of methyl ether of β -naphthol.

o-nitro benzal di- β -naphthol dimethyl ether.- The residue weighed 1.95 g. (M.P. - $194-6^{\circ}$)

Only a faint odor of methyl ether of β -naphthol could be detected.

β -phenyl propional di- β -naphthol dimethyl ether.- A yellow resinous substance remained in the distillation flask which was not purified.

Methyl ether of β -naphthol (0.52 g.) was isolated from the distillate.

Di- β -naphthol methane dimethyl ether.- The crystalline residue weighed 1.86 g. - M.P. - $136-42^{\circ}$. After several crystallizations from alcohol, the mixture was shown to consist chiefly of the starting material.

The distillate contained 0.10 g. of the methyl ether of β -naphthol.

Trichloroacetal di- β -naphthol dimethyl ether.- Five-tenths of a gram of the substance were subjected to the treatment previously described, and 0.47 g. were recovered.

No methyl ether of β -naphthol could be detected.

The Dinaphthopyrans:

Samples (0.5 g.) of benzal and anisal di- β -naphthyl ethers were quantitatively recovered after treatment with two percent hydrochloric acid.

The Tetra-aryl Methanes:

No triphenyl carbinol could be isolated following the previously described treatment with two percent hydrochloric acid, of any of the four substances examined.

REACTIONS WITH THE ANTI-DIAZOTATE OF 2,5 DICHLORANILINE

Five-tenths of a gram of each substance investigated were dissolved in 50 c.c. of glacial acetic acid and the solutions were cooled to room temperature. Twenty c.c. of water, containing four moles of the diazotate for each mole of compound, were added dropwise to the agitated solutions. After five to seven minutes, the red precipitates were collected on filters washed with 50% acetic acid and water. The weights and melting points of the products have been recorded in Table 2.

One gram of triphenyl methyl naphthol yielded 1.50 g. of a red substance. (M.P. - $265-73^{\circ}$) After crystallization from pyridine-methyl alcohol, the M.P. $275-7^{\circ}$ was obtained.

Anal. Calcd. for $C_{35}H_{24}ON_2Cl_2$: N, 5.01

Found: N, 5.00

SUMMARY

1. The validity of the general theory of the stability of the carbon-to-carbon bond has been given further experimental confirmation in the case of markedly polar carbon-to-carbon bonds.

2. Carbon-to-carbon bonds have been formed which possess the remarkable property of undergoing hydrolytic scission in the presence of dilute mineral acids.

3. The following new compounds have been prepared:

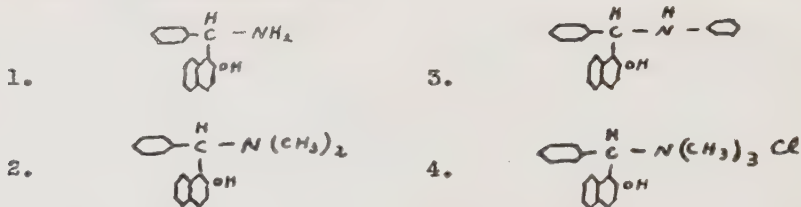
- (1) $(p\text{-CH}_3O\cdot C_6H_4)\text{-CH:} (\beta\text{-C}_{10}H_6OH)_2$ anisal di- β -naphthol
- (2) $(p\text{-CH}_3O\cdot C_6H_4)\text{-CH:} (\alpha\text{-C}_{10}H_6OCH_3)_2$ anisal di- β -naphthol dimethyl ether
- (3) $(C_6H_5)\text{-CH:} (\beta\text{-C}_{10}H_6OCH_3)_2$ benzal di- β -naphthol dimethyl ether
- (4) $(C_6H_5\cdot C_2H_4)\text{-CH:} (\beta\text{-C}_{10}H_6OH)_2$ β -phenyl propional di- β -naphthol
- (5) $(C_6H_5\cdot C_2H_4)\text{-CH:} (\beta\text{-C}_{10}H_6OCH_3)_2$ β -phenyl propional di- β -naphthol dimethyl ether
- (6) $(C_6H_5\cdot C_2H_4)\text{-CH:} (\beta\text{-C}_{20}H_{12}O)$ β -phenyl propional di- β -naphthyl ether
- (7) $(p\text{-(CH}_3)_2N\cdot C_6H_4)\text{-CH:} (\beta\text{-C}_{10}H_6OH)_2$ p-dimethylamino benzal di- β -naphthol
- (8) $(Cl_3C)\text{-CH:} (\beta\text{-C}_{10}H_6OCH_3)_2$ trichloroacetal di- β -naphthol dimethyl ether
- (9) $(C_6H_5)_3C\text{-(}\beta\text{-C}_{10}H_6OH\text{)-N}_2\text{-(2,5-C}_6H_3Cl_2\text{)}$ triphenyl-methyl, 2,5 dichlorobenzene azo, β -naphthol

II. THE INFLUENCE OF SALT FORMATION ON THE STABILITY OF THE
CARBON-TO-NITROGEN BOND OF CERTAIN
SUBSTITUTED METHYL AMINES

During an investigation of the hydrolytic stability of the carbon-to-nitrogen bond in molecules of the type $\text{R}-\overset{\text{H}}{\underset{\text{OH}}{\text{C}}}-\text{NH}_2$, Kharasch and Howard⁹ observed that molecules of that type are unaffected by boiling with twenty percent hydrochloric acid, whereas boiling with .05 N. hydrochloric acid produced extensive hydrolysis. The difference in the behavior of these substances in concentrated and dilute acids is attributed to two factors:

1. The insolubility of the amine hydrochlorides in strongly acid solutions.
2. The decrease in the electronegativity of the amino group by virtue of its being in the form of a salt.

The purpose of this investigation was to examine the validity of the second factor by comparing the rates of hydrolysis of the following molecules:

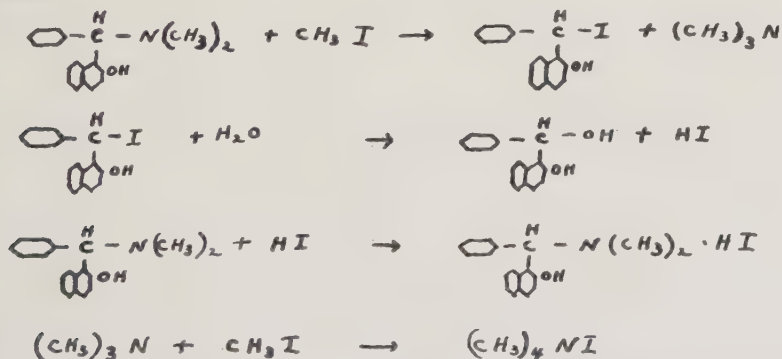


Phenyl β -naphthol methyl dimethyl amine was studied as a means of demonstrating that by increasing the basicity of the nitrogen atom, the stability of the hydrochloride is increased, and that, as a result of the decreased concentration of the base, a

decreased rate of hydrolysis results. It was hoped that phenyl β -naphthol methyl trimethyl ammonium chloride could be synthesized in order to obtain additional evidence for the stabilizing effect of salt formation on molecules of this type. Phenyl β -naphthol methyl aniline was prepared for the purpose of studying the effect of weakening the basicity of the amino group.

RESULTS

All attempts to prepare phenyl β -naphthol methyl trimethyl ammonium iodide by the action of methyl iodide on the tertiary amine failed. The chief products of the reaction were: tetramethyl ammonium iodide and phenyl β -naphthol methyl dimethyl amine hydro-iodide. These products suggest the following reactions:



The stabilizing effect of attaching two methyl groups to the nitrogen atom is strikingly shown by comparing the extent of hydrolysis of two g. samples of compounds 1. and 2. in .01 N. hydrochloric acid at 100°. Eight hundred milligrams of phenyl β -naphthol methyl ammonium chloride were recovered after seventy-five minutes, as compared with 1.2 g. of phenyl β -naphthol methyl dimethyl ammonium chloride.

Phenyl β -naphthol methyl aniline, on the other hand, was rapidly and completely decomposed by boiling 20% hydrochloric

acid - conditions under which the other two amines are very stable.

EXPERIMENTAL PART

PREPARATIONS

Phenyl β -naphthol methyl amine:

This amine and its hydrochloride were prepared according to the method of Betti.²¹

Phenyl β -naphthol methyl dimethyl amine:

The method of Littman and Brode²² was utilized for the preparation of the amine and its hydrochloride.

Phenyl β -naphthol methyl aniline:

This compound was prepared according to the directions of Betti.²³

Action of methyl iodide on phenyl β -naphthol methyl dimethyl amine:

All experiments were carried out in evacuated bomb tubes at 100°.

1. Ten g. of the amine with 10 g. of methyl iodide yielded a red-brown gum after heating for three hours. Successive triturations with acetone left a small amount of a yellow powder containing iodine. This material was dissolved in 50% acetone and shaken with ten moles of silver chloride for several hours. The acetone-water mixture was evaporated to dryness in vacuo leaving a white powder - M.P. - 175-85°. (dec.) After a series of crystallizations from anhydrous methyl alcohol-ether mixtures, it was identified as the hydrochloride of phenyl β -naphthol methyl dimethyl amine - M.P. - 210°.

2. One g. of the amine, one c.c. of methyl iodide and

21. Betti, Organic Syntheses, 9, 60 (1929)

22. Littman and Brode, J. Am. Chem. Soc., 52, 1657 (1930)

23. Betti, Gazz. Chim. Ital., 33 II, 303 (1900)

15 c.c. of acetone were heated together for three hours. A white crystalline substance (0.22 g.) was obtained by cooling the solution. The material charred somewhat at about 170° but did not melt below 300° . It contained 43.4% iodine. The acetone solution yielded a gum which was extracted with warm benzene. The residue was a yellow powder - M.P. - 175° . (dec.) It contained 26.9% iodine and was decomposed by dilute ammonium hydroxide.

3. A similar experiment with 5 c.c. of acetonitrile as the solvent yielded 0.3 g. of shiny leaflets which did not melt below 300° . The substance contained 60.5% of iodine. (Calcd. for tetramethyl ammonium iodide, 63.2%) The acetonitrile contained a small amount of the hydro-iodide of the amine.

HYDROLYSES

Phenyl β -naphthol methyl amine:

Two g. of the amine hydrochloride were dissolved in 125 c.c. of boiling water containing 0.12 c.c. of concentrated hydrochloric acid. The solution was subjected to steam distillation for seventy-five minutes.

A trace of insoluble material - M.P. - $175-90^{\circ}$ - was formed. Four hundred milligrams of β -naphthol were obtained by filtration of the cooled dilute hydrochloric acid. Evaporation of the filtrate left a crystalline residue which was triturated with benzene to remove the trace of β -naphthol present. The purified residue weighed 0.8 g. and was identified as phenyl β -naphthol methyl amine hydrochloride.

Seven-tenths of a g. of a red dye - M.P. - $120-45^{\circ}$ (dec.) were obtained by treatment of the distillate with an excess of the anti-diazotate of 2,5 dichloraniline.

Phenyl β -naphthol methyl dimethyl amine:

The same treatment was applied to 2 g. of the amine hydrochloride. One and two-tenths g. of unchanged material were recovered. A small quantity (0.15 g.) of benzal di- β -naphthol was isolated from the insoluble gum remaining in the distillation flask. Fifty milligrams of β -naphthol were obtained by cooling the reaction mixture and an additional amount was isolated from the distillate as 2,5 dichlorobenzene azo β -naphthol.

Phenyl β -naphthol methyl aniline:

One and one-tenth g. of the amine were dissolved in a mixture of 25 c.c. of alcohol and 25 c.c. of acetone. The solution was added dropwise to 125 c.c. of boiling 20% hydrochloric acid through which a rapid current of steam was passing. Distillation was continued for one hour.

A brown gum collected on the walls of the flask. Treatment with acetone-alkali permitted the isolation of 0.3 g. of benzal di- β -naphthol. Evaporation of the hydrochloric acid left 0.4 g. of a red residue. After trituration with benzene, 0.35 g. remained. (M.P. - $189-93^{\circ}$) The melting point of a mixture of the residue and aniline hydrochloride was $190-3^{\circ}$.

Three hundred milligrams of 2,5 dichlorobenzene azo β -naphthol were obtained from the filtrate.

SUMMARY

Experimental evidence has been obtained which indicates that the basicity of the amine is an important factor in determining the rate of hydrolysis in acid solution.

